THE ADDITION OF HYDROGEN CHLORIDE TO ALLYL DIMETHYLAMINE IN THE MOLTEN STATE

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When a benzene solution of dimethylamine carbonate was acted upon by allyl chloride, the product was allyl dimethylamine; addition of hydrogen chloride into the molten hydrochloride of the latter compound furnished 3-chloropropyl dimethylamine.

The hydrogen halide addition to N-substituted allylamine systems has been investigated by KHARASCH and FUCHS (1) under various conditions. The addition of gaseous hydrogen chloride to the molten hydrochloride of allyl diethylamine resulted in the formation of an isomeric mixture of 2- and 3-chloropropyl diethylamine. This method gave a higher yield of the 3-chloropropyl diethylamine isomer then the method of using concentrated aqueous hydrochloric acid under pressure.

$$CH_2=CH-CH_2-N(CH_3)_2 \,.\, HCl \xrightarrow[160^\circ]{HCl} Cl-CH_2-CH_2-CH_2-N(CH_3)_2$$

In the present work the HCl addition to molten allyl dimethylamine-hydrochloride was attempted. The preparation of allyl dimethylamine as described by WESTON and his coworkers (2) as well as by COPE and TOWLE (3), consisted of reacting dimethylamine with allyl chloride under pressure. Furthermore, the base was prepared from allyl bromide by PARTHELL and BROICH (4), and from allyl iodide by KNORR and ROTH (5).

In our experiments, allyl dimethylamine was prepared in a satisfactory yield from allyl chloride by reacting it either with the benzene solution of dimethylamine carbonate or with aqueous dimethylamine solution without pressure.

The addition of hydrogen chloride to molten allyl dimethylamine hydrochloride resulted in the formation of 3-chloropropyl dimethylamine. According to the method of KHARASCH, the addition is carried out by passing dry hydrogen chloride over the surface of the melt instead of this procedure, however, it seemed more suitable to bubble the gas through molten material, thus ensuring a larger contacting surface of the components of the heterogeneous reaction mixture.

After having completed the addition, the base could be liberated from the formed 3-chloropropyl dimethylamine hydrochloride by concentrated sodium hyd-

roxide solution. It is noteworthy that while similar treatment of allyl diethylamine (1) gave a mixture of 2- and 3-chloroisomers, allyl dimethylamine yielded in our experiments only the 3-chloroisomer, and a single fractionated distillation of the base on a usual column afforded a product of satisfactory purity.

Experiments of hydrogen chloride addition were attempted also in dimethylformamide solution in the presence of benzoyl peroxide, but under such conditions no addition took place, and onby the unreacted starting material could be recovered.

Experimental

Allyl dimethylamine hydrochloride. 50 g (47 ml, 0,66 mol) allyl chloride was mixed with 384 ml of a benzene solution of dimethylamine carbonate, containing 60 g (1,33 mol) of dimethylamine. After having allowed the mixture to stand half an hour, it was gently refluxed for an hour on a steam-bath. After 24 hours' standing at room temperature, the separated crystals were filtered off and washed with some anhydrous benzene. The combined filtrate and washing liquid were distilled in a water-bath under atmospheric pressure. The distillate was extracted with 200 ml of 2 N HCl in several portions and the combined aqueous extract was evaporated to dryness under reduced pressure. The yield was 61,2 g (77%) of hygroscopic allyl dimethylamine hydrochloride.

Allyl dimethylamine (base). a) 26,6 g (25 ml 0,35 mol) of allyl chloride and 208 ml of a benzene solution of dimethylamine carbonate (15,43 g) dimethylamine in 100 ml benzene were mixed; after standing 24 hours, the mixture was glutly refluxed, then after cooling again 52 ml dimethylamine solution of the above concentration was added, and the mixture was allowed to stand 24 hours at room temperature. The separated crystals were filtered, and washed with some anhydrous benzene. The filtrate was combined with the washing liquid, and distilled under atmospheric pressure on a water-bath. The distillate was fractionally extracted with 200 ml of 2 N HCl. The combined aqueous extracts were evaporated to dryness under reduced pressure, and treated with 100 ml 50% NaOH solution. The separated organic layer after drying over anhydrous sodium sulphate was fractionated at atmospheric pressure. B. p. 60—64°; 10,5 g. (40%), $n_D^{25,3} = 1{,}3980$

(Data in literature: b. p. 61—64° C (2); $n_D^{25} = 1{,}3981$(3).
Analysis: ($C_5H_{11}N$) Calculated C 70,53 H 13,02 N 16,45;
Found C 70,62 H 13,10 N 16,61.

b) 50 g of allyl chloride (47 ml, 0,66 mol) and 150 ml of aqueous dimethylamine solution (40 g dimethylamine in 100 ml) were mixed under cooling. The reaction mixture was homogenized by adding 40 ml ethanol in portions and shaking. After 24 hours' standing the reaction mixture was refluxed for an an hour, then allowed again to stand 24 hours. After filtration the mixture was acidified with concentrated hydrochloric acid under intensive cooling then the acidic solution was evaporated under reduced pressure. The obtained syrupy residue was treated with 150 ml 50% NaOH, the organic layer separated, and after drying (Na_2SO_4 sicc.) fractionated under atmospheric pressure.

B. p. 60°, $n_D^{22} = 1{,}3991$ 22,6 g (41%).

3-chloropropyl dimethylamine (base) *a*) 51,4 g. of allyl dimethylamine hydrochloride was melted at 155—160°, and a stream of dry hydrogen chloride was passed through it for 24 hours. Weight increase was 7 g. The substance thus obtained was dissolved in 25 ml water, saturated with K_2CO_3, and filtered. The filtrate was extracted with 10×100 ml ether, while the salt remaining on the filter was previously washed with the single ether portions. After drying over anhydrous Na_2SO_4, the combined ether extracts were fractionated.

B. p. $_{50}$: 51—53°, 12,1 g. (23%), $n_D^{20} = 1{,}4314$
(Data in literature: b. p. $_{50}$: 51—53° (6), n_D^{20} : 1,4313 (7).

Analysis ($C_5H_{12}NCl$)	Calculated	C 49,38	H 9,94	N 11,52	Cl 29,15
	Found	C 49,47	H 9,87	N 11,69	Cl 29,23

Picrate prepared in the usual way in abs. ethanol solution. M. p. 109—110° (Data in literature 109,8—110,1° [6]).

Analysis ($C_{11}H_{15}O_7N_4Cl$)	Calculated	C 37,66	H 4,31	N 15,97
	Found	C 37,70	H 4,42	N 16,08.

b) Dry hydrogen chloride was introduced into 49,7 g allyl dimethylamine base under cooling. The reaction mixture became considerably warm, then it froze to give a white crystalline mass. Thereafter it was heated to 155—160° while continuing the introduction of HCl gas. After 12 hours of gas-introduction the increase of weight was 40,6 g (95,1%). The cooled product was dissolved in 50 ml water, treated with decolourizing carbon, and mixed with 100 ml 50% NaOH while cooling in icewater. The organic layer was separated, dried over Na_2SO_4 and fractionated.

B. p. $_{50}$: 51—54°, 20,6 g. (30%) n_D^{21} : 1,4310

Picrate prepared in the above way. M. p. 109—110°.

Attempted HCl-addition in dimethylformamide solution

100 g of allyl dimethylamine hydrochloride was dissolved in 200 ml of freshly distilled dimethylformamide. Dry HCl-gas was bubbled through the cooled solution for 6 hours. Then dimethyl formamide was distilled off at 10 mm pressure, and the crystalline residue treated with 200 ml 50% NaOH solution. The organic layer was separated, dried over Na_2SO_4, and fractioned under atmospheric pressure. B. p. 61—64°, 22,6 g. (37%), n_D^{23} : 1,3993 corresponding to the properties of the allyl dimethylamine base. No 3-chloropropyl dimethylamine could be isolated.

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ПРИСОЕДИНЕНИЕ ХЛОРИСТОГО ВОДОРОДА К АЛЛИЛДИМЕТИЛАМИН В ПЛАВАХ

М. Халмош, Т. Мохачи и Дь. Ченгери

Реакция аллилхлорида с бензольным раствором диметиламинкарбоната ведет к аллилдиметиламину. Путем присоединения хлористого водорода в плавах гидрохлорида последнего 3-хлорпропилдиметиламин получается.